

# Bowl-Shaped Hydrocarbons Related to C<sub>60</sub>

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**ABSTRACT:** *Ab initio* studies at the HF/6-31G\* and B3LYP/6-31G\* levels are reported for two bowl-shaped hydrocarbons related to C<sub>60</sub>: C<sub>30</sub>H<sub>12</sub> and C<sub>36</sub>H<sub>12</sub>, of C<sub>3</sub> and C<sub>3v</sub> symmetry, respectively. The former has an approximate heat of formation of 211 kcal/mol. Bowl-to-bowl interconversion may occur through a planar (C<sub>3h</sub>) form of ca. 64 kcal/mol greater energy having one imaginary vibrational frequency. The larger C<sub>36</sub>H<sub>12</sub> bowl has a calculated  $\Delta H_f^\circ$  of 265 kcal/mol. Its HF/6-31G\*, B3LYP/6-31G\*, and MM3 bond lengths are in good agreement with a recent X-ray structure. Chemical shifts for both compounds calculated by the GIAO method are in good agreement with the measured NMR spectra. The observed <sup>13</sup>C chemical shifts increase with the extent of pyramidalization. © 1998 John Wiley & Sons, Inc. *J Comput Chem* 19: 189–194, 1998

**Keywords:** fullerene, *ab initio*; carbon-13; nuclear magnetic resonance; density functional; buckyball; MM3

## Introduction

The discovery and characterization of fullerenes have revived interest in bowl-shaped hydrocarbons, an area of research which had been dormant since the remarkable preparation of corannulene by Barth and Lawton more

than 30 years ago.<sup>1</sup> The renaissance in the study of nonplanar hydrocarbon fragments includes those that do (“buckybowls”) and do not map onto C<sub>60</sub> or other fullerenes. Several recent reviews have investigated bowl-shaped fullerene fragments.<sup>2</sup>

Nonplanar pi-systems, such as the buckybowls, are potential precursors to fullerenes and larger nonplanar pi-systems. Perhaps more important, they have accessible concave and convex surfaces, the chemistries of which may differ. To increase our understanding of these fragments, buckybowls 1 and 2 are investigated by means of *ab initio*

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calculation to obtain estimates of heats of formation and NMR chemical shifts; the latter permit assignment of the observed spectra. It is found that the  $^{13}\text{C}$  chemical shifts increase with the extent of carbon pyramidalization.

## Methods

*Ab initio* SCF and B3LYP<sup>3</sup> density functional calculations, with geometry optimization, were performed in the 6-31G\* basis set<sup>4</sup> with Gaussian-94<sup>5</sup> on Digital Alpha AXP 2100 servers and Iris indigo workstations.  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts were calculated by the GIAO method<sup>6</sup> at the HF/6-31G\* level.

## Triindenotriphenylene

The title compound of this section, **1**, a benz-*as*-indacenoindenchrysene, is a  $\text{C}_{30}\text{H}_{12}$  hydrocarbon containing three five-membered rings and seven six-membered rings. It has recently been synthesized by Abdourazak et al.,<sup>7</sup> and shortly thereafter, in higher yield, by Hagen et al.<sup>8</sup>

Calculations at the HF/6-31G\* and B3LYP/6-31G\* levels furnish a structure having  $\text{C}_3$  symmetry (Fig. 1). Its HF and B3LYP energies are  $-1142.98819$  and  $-1150.38127$  hartrees (h), respectively, and its dipole moment is 3.9 (HF) and 3.4 D (B3LYP), with negative end toward the benzene

base. The HF/6-31G\*\* energy is  $-1143.00958$  h. The bond lengths of **1**, corresponding to the numbering in Figure 2, are given in Table I. They vary from 1.357 to 1.522 Å in HF/6-31G\* and from 1.379 to 1.513 Å in B3LYP/6-31G\*. The greatest bond length is found for  $\text{C}_{3a}\text{C}_{3b}$ , a single bond in all Kekulé structures.

Faust and Vollhardt have studied both triindenotriphenylene **1** and its planar  $\text{C}_{3h}$  form **1a** using the MNDO method.<sup>9</sup> They find that the planar form lies 77.3 kcal/mol above the bowl. Our HF/6-31G\* and B3LYP/6-31G\* calculations lead to a  $\text{C}_{3h}$  structure for **1a** having one imaginary frequency ( $127.5i$ ,  $\text{A}''$ ) in HF/6-31G\*. The HF/6-31G\* and B3LYP/6-31G\* energies of **1a** are  $-1142.88067$  and  $-1150.28025$ , giving an energy difference relative to **1** of 67.5 (HF) and 63.3 (B3LYP) kcal/mol. We obtain 67.6 kcal/mol at the HF/6-31G\*\* level. (Sygula and Rabideau<sup>10</sup> report that the HF/6-31G\* energy of the  $\text{C}_{3h}$  structure is 68.4 kcal/mol higher than that of the bowl.) As seen from Table I, the  $\text{C}_{3a}\text{C}_{3b}$  bond length of **1a** increases to 1.642 Å (HF) and 1.640 Å (B3LYP).

The calculated chemical shifts ( $\delta$  in ppm from TMS), Table II, are in good agreement with the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra,<sup>7</sup> allowing several remaining assignments to be made. The four observed proton resonances for each set of three hydrogens include a singlet (7.85), two doublets (7.62 and 7.67), and a doublet of doublets (7.39), with the singlet corresponding to  $\text{H}_4$  and the doublet of doublets to  $\text{H}_2$ . The calculated proton shifts are 8.0, 7.6, 8.0, and 8.2 for  $\text{H}_1$ ,  $\text{H}_2$ ,  $\text{H}_3$ , and  $\text{H}_4$ , respectively. The

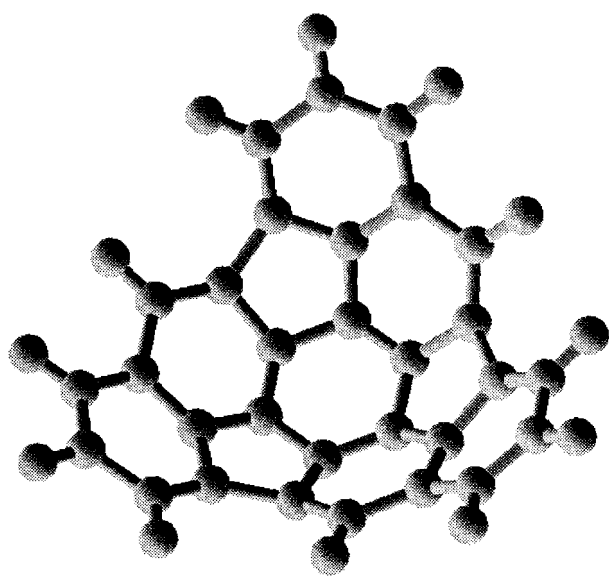


FIGURE 1. Bowl-shaped  $\text{C}_{30}\text{H}_{12}$ , **1**.

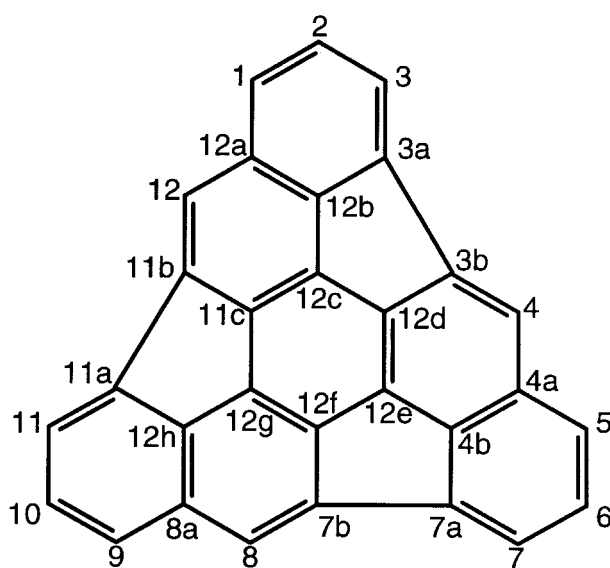


FIGURE 2. Numbered diagram of **1**.

**TABLE I.**  
**Bond Lengths (Å) of 1 (C<sub>3</sub>) and 1a (C<sub>3h</sub>).**

Bond	C <sub>3</sub>		C <sub>3h</sub>	
	HF / 6-31G*	B3LYP / 6-31G*	HF / 6-31G*	B3LYP / 6-31G*
1—2	1.372	1.391	1.381	1.402
2—3	1.423	1.423	1.446	1.443
3—3a	1.365	1.385	1.365	1.386
3a—3b	1.522	1.513	1.642	1.640
3b—4	1.370	1.392	1.403	1.427
4—4a	1.461	1.457	1.520	1.516
4a—5	1.421	1.424	1.431	1.431
3a—12b	1.428	1.435	1.445	1.449
3b—12d	1.436	1.443	1.399	1.404
4a—4b	1.391	1.413	1.390	1.414
12b—12c	1.400	1.406	1.347	1.352
12c—12d	1.421	1.428	1.371	1.377
12d—12e	1.357	1.379	1.322	1.340

chemical shifts of the two doublets at 7.62 and 7.67, for H<sub>1</sub> and H<sub>3</sub>, are both calculated to be 8.0 ppm. The calculated proton shifts are in the experimental order and exceed the observed values by only 0.2–0.4 ppm.

Ten distinct <sup>13</sup>C resonances were observed for compound 1: δ 120.7, 125.0, 127.4, 128.3, 135.4, 138.2, 138.6, 144.9, 148.3, and 153.1. The first four of these were assigned to the H-bearing carbons, for which the calculated shifts are as follows: C<sub>1</sub>, 127.0; C<sub>2</sub>, 124.7; C<sub>3</sub>, 121.1; and C<sub>4</sub>, 125.9. The smallest chemical shift is found for C<sub>3</sub>, whereas the other three shifts are more typical of benzenoid carbons and similar to that calculated for corannulene, 125.2 ppm. The three shifts for the remaining

peripheral carbons are higher: C<sub>3a</sub>, 136.9; C<sub>3b</sub>, 142.4; C<sub>4a</sub>, 132.7, and probably correspond to the observed chemical shifts at 138.2, 144.9, and 135.4 ppm. Finally, the internal carbons have the following chemical shifts: C<sub>12b</sub>, 139.4; C<sub>12c</sub>, 146.1; C<sub>11c</sub>, 153.1, corresponding to the observed values 138.6, 148.3, and 153.1. The largest values correspond to the benzene carbons in the bowl's hexagonal base. These chemical shifts increase roughly in the same order as the corresponding POAV1 pyramidalization angles.<sup>7,11</sup>

## Triacenaphthyltriphenylene

The incorporation of three additional ethylene moieties in 1 results in 2, a C<sub>36</sub>H<sub>12</sub> bowl-shaped fragment of C<sub>3v</sub> symmetry. Two views of it are shown in Figure 3 and its numbering scheme in Figure 4. This molecule was recently synthesized by Scott et al., who obtained its NMR spectrum in CDCl<sub>3</sub>.<sup>12</sup> We have optimized it at the HF/6-31G\* and B3LYP/6-31G\* levels, obtaining the bowl-shaped structure depicted in Figure 3 and energies of −1370.18787 and −1379.01191 h, respectively. The molecule has a dipole moment of 5.2 D (HF) and 4.6 D (B3LYP), with the negative end directed toward the benzene base. At the HF/6-31G\* level, the energy of the doubly degenerate HOMO, −0.275 h, is comparable to that computed for 1, −0.271 h; the degenerate LUMO energy is 0.045 h, slightly smaller than the 0.057 h found for 1. (The nondegenerate virtual orbital above the LUMO has an energy of 0.070 h). The HOMO–LUMO gap of

**TABLE II.**  
**<sup>13</sup>C Chemical Shifts and POAV1 Angles of 1.**

Carbon	Calculated <sup>a</sup>	Experiment <sup>b</sup>	POAV1 angle <sup>c</sup>
C <sub>1</sub>	127.0	128.3	0.9
C <sub>2</sub>	124.7	125.0	1.6
C <sub>3</sub>	121.1	120.7	1.2
C <sub>4</sub>	125.9	127.4	3.7
C <sub>3a</sub>	136.9	138.2	5.1
C <sub>3b</sub>	142.4	144.9	7.5
C <sub>4a</sub>	132.7	135.4	4.6
C <sub>11c</sub>	153.1	153.1	10.1
C <sub>12c</sub>	146.1	148.3	10.7
C <sub>12b</sub>	139.4	138.6	6.5

<sup>a</sup> GIAO / 6-31G\* values in ppm relative to TMS.

<sup>b</sup> Measured in CDCl<sub>3</sub>, ref. 7.

<sup>c</sup> POAV1 angle θ − 90 (in degrees).

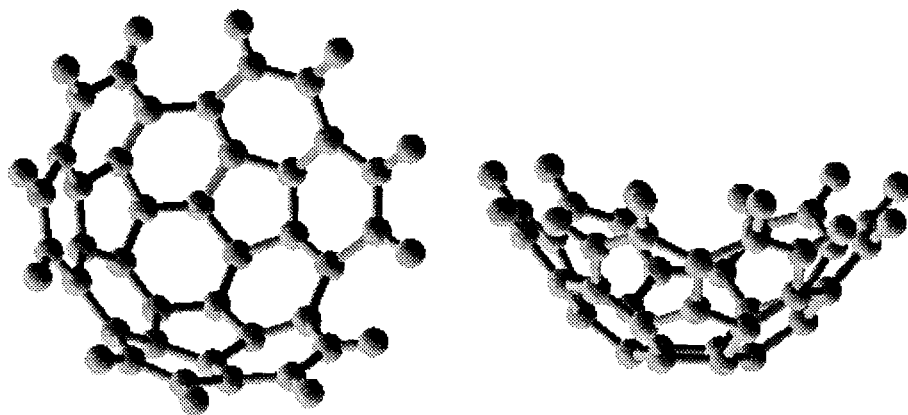


FIGURE 3. Two views of the  $C_{36}H_{12}$  structure **2** obtained at HF / 6-31G\*.

**2**, 8.7 eV, is slightly smaller than that calculated for **1**, 8.9 eV, and both are less than that of corannulene, 9.7 eV. Thus, **1** and **2**, like corannulene, may be capable of four-electron reductions.

The HF/6-31G\* bond lengths of **2**, given in Table III, range from 1.358 to 1.476 Å, the latter for  $C_{2a}C_{2b}$ . These bond lengths are in good agreement with the X-ray values,<sup>13</sup> as are those obtained from MM3.<sup>14</sup> The pattern of bond lengths is consistent with the Kekulé structure given in Figure 4, where all double bonds are exocyclic to the five-membered rings. Thus, the hexagonal base of **2**, like that of **1**, shows significant cyclohexatriene-like bond alternation.

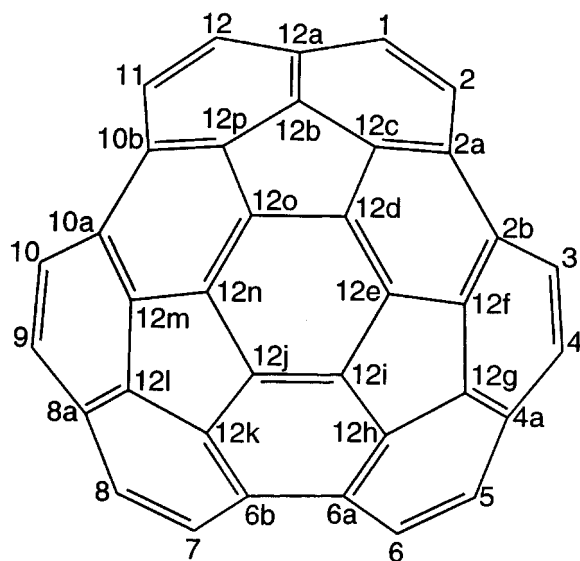


FIGURE 4. Numbered diagram of **2**.

The proton NMR spectrum of **2** shows doublets at 7.20 and 7.58 ppm. The calculated proton resonances are 7.84 and 7.46 for  $H_1$  and  $H_2$ , respectively. The calculated  $^{13}C$  resonances (Table IV) are in agreement with the observed values:  $\delta$  152.2, 139.4, 136.8, 135.1, 127.2, 126.8, and 125.4. The signals at 127.2 and 125.4, identified with hydrogen-bearing carbons, are calculated to be:  $C_1$ , 124.9,  $C_2$ , 124.1. The signal at  $\delta$  152.2 can be assigned to the carbons of the hexagonal base, calculated to be 154.8. The calculated resonances for the remaining peripheral carbons ( $C_{12a}$ , 126.1;  $C_{2a}$ , 135.3) can be identified with the signals at 126.8 ppm and 135.1. Finally, the remaining two signals,  $\delta$  136.8 and 139.4, probably correspond to the interior carbons, calculated to be:  $C_{12b}$ , 136.1;  $C_{12c}$ , 139.8.

TABLE III.  
Bond Lengths (Å) of **2**.

Bond	MM3 <sup>a</sup>	HF <sup>b</sup>	B3LYP <sup>b</sup>	X-ray <sup>c</sup>
1—2	1.379	1.362	1.382	1.375, 1.385
1—12a	1.444	1.442	1.440	1.430, 1.427
2—2a	1.453	1.448	1.445	1.436, 1.445
2a—12c	1.398	1.383	1.407	1.393, 1.396
12a—12b	1.380	1.366	1.391	1.382
12b—12c	1.436	1.436	1.437	1.438, 1.439
2a—2b	1.464	1.476	1.477	1.472
12c—12d	1.436	1.430	1.436	1.430
12d—12e	1.381	1.358	1.380	1.379
12d—12o	1.450	1.435	1.442	1.430

<sup>a</sup> Ref. 14.

<sup>b</sup> In the 6-31G\* basis.

<sup>c</sup> Ref. 13.

**TABLE IV.**  
**<sup>13</sup>C Chemical Shifts and POAV1 Angles of 2.**

Carbon	Calculated <sup>a</sup>	Experiment <sup>b</sup>	POAV1 angle <sup>c</sup>
C <sub>1</sub>	124.9	127.2	2.1
C <sub>2</sub>	124.1	125.4	1.5
C <sub>2a</sub>	135.3	135.1	6.2
C <sub>12a</sub>	126.1	126.8	4.5
C <sub>12b</sub>	136.1	136.8	8.9
C <sub>12c</sub>	139.8	139.4	9.7
C <sub>12d</sub>	154.8	152.2	12.0

<sup>a</sup> GIAO/6-31G\* values in ppm relative to TMS.<sup>b</sup> Measured in CDCl<sub>3</sub>.<sup>12</sup><sup>c</sup> POAV1 angle  $\Theta - 90$  (in degrees).

## Heats of Formation

The method of group equivalents calculates the  $\Delta H_f^\circ$  of **1** and **2** as the difference between the *ab initio* energies and the sum of group equivalents (GEs) for the  $=C_b\langle$  and  $=C_bH-$  moieties in each molecule.

A GE ( $=C_bH-$ ) of  $-38.45576$  h is available from studies on planar aromatics at the HF/6-31G\* level.<sup>15</sup> In this work, a GE ( $=C_b\langle$ ) suitable for bowl-shaped hydrocarbons,  $-37.88086$  h, was obtained from the energy of corannulene,  $-763.18928$  h, and its experimental  $\Delta H_f^\circ$ , 111 kcal/mol.<sup>16</sup>

Use of these group equivalents and the HF/6-31G\* energies for **1** and **2**,  $-1142.98819$  and  $-1370.18787$  h, leads to  $\Delta H_f^\circ$  values of 211 and 265 kcal/mol for **1** and **2**, respectively. Similar heats of formation are found using MM3: 213 and 260 kcal/mol.

## Conclusions

The *ab initio* HF and B3LYP energy differences between **1** and the putative transition state **1a** are the same to within 1.2 kcal/mol, indicating that correlation effects play a small role in determining the barrier height. We have also observed this to be the case in corannulene.

The *ab initio* heats of formation of **1** and **2** are 211 and 265 kcal/mol. The increase in  $\Delta H_f^\circ$  for incorporation of the six additional strained carbon atoms is 54 kcal/mol or 9 kcal/mol  $\cdot$  C, approaching the per-carbon  $\Delta H_f^\circ$  of 10 kcal/mol in C<sub>60</sub>.

The <sup>13</sup>C chemical shifts in **1** and **2** increase with increasing POAV1 angle, reflecting the rehybridization and increased s-character at those carbons. A striking example is found for the calculated shifts of **1** and (planar) **1a**: the carbons of the base, C<sub>11c</sub> and C<sub>12c</sub>, have  $\delta$  153.1 and 146.1 in **1**, and much smaller values, 120.5 and 119.5, in **1a**.

The largest measured chemical shifts of **1** and **2**,  $\delta$  153.1 and 152.2, exceed those of C<sub>60</sub>, 143,<sup>17</sup> and the more shallow corannulene, 135.8,<sup>18</sup> which have POAV1 angles of 11.6° and 8.4°, respectively.

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